(54) CONTROLLED OXIDATION OF ETHYLENE

(71) We, HALCON INTERNATIONAL INC., of 2 Park Avenue, New York 16, New York, United States of America, a corporation organized and existing under the Laws of the State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement: —

This invention relates to the production of ethylene oxide. More particularly, the invention relates to the silver catalyzed controlled oxidation of ethylene to ethylene oxide by the use of reaction feed gas wherein ethane is a substantial component, i.e., wherein ethane represents at least about 10 mol % of the total gas feed to the reaction zone.

It is well-known that the silver catalyzed oxidation of ethylene to ethylene oxide with molecular oxygen can be controlled by the employment of diluents, such as, nitrogen, carbon dioxide, steam and other gaseous materials, inert under the conditions of the reaction, in the reaction zone. However, while some degree of control is thereby maintained over the reaction, and controlled oxidation of ethylene to ethylene oxide may be effected, the conversion of ethylene and the selectivity of the reaction are such that there is room for considerable improvement.

It is taught in the prior art that the presence of methane in the diluent material may permit additional control with the attendant advantage of improved efficiency. However, even this process suffers from the disadvantage of requiring substantially pure ethylene feedstock since the inclusion of other normally present saturated hydrocarbons, such as ethane, are regarded as particularly harmful to the selectivity of the reaction and as exerting a decidedly depressing effect upon ethylene oxide yield. In point of fact, the prior art goes far beyond conjecture and offers seemingly clear and convincing empirical data to support its adamant position that optimum production rate is achieved in the total absence of ethane and that as the ethane content of the total feed to the reactor is increased, the production rate is substantially decreased (note U.S. patent No. 3,119,837). It is also taught in the prior art that ethane causes reduced production rates and should be maintained below 1 mol % and preferably below 0.2 mol % of the reaction feed. Accordingly, even in those ethylene oxide processes wherein oxidation is effected with high purity oxygen, i.e., at least about 85 mol %, small quantities of ethane in the ethylene feedstock were deemed to be detrimental in that the overall yield of ethylene oxide product was thereby substantially reduced. Generally, minimization of ethane in ethylene feed is effected by the installation of auxiliary scrubbing equipment for removal of paraffins from the feed ethylene. The cost of such installation and equipment and the operation thereof impose a significant economic penalty on the manufacture. Other removal treatments may comprise such unit operations as distillation, absorption, adsorption, extraction, and the like. It has also been suggested that molecular sieves, such as the highly porous adsorbents composed of crystalline sodium and calcium alumino-silicates, after heating to remove water of hydration, be employed to preferentially adsorb ethylene and thereafter strip the adsorbed ethylene for recycle by means of an inert gas at elevated temperature. Whatever the technique employed it is apparent that additional equipment and processing operations are required which impair the efficiency and economy of the overall ethylene oxide process.

In prior art ethylene oxide processes of the type hereinabove discussed, the use of inhibitors to retard complete combustion of ethylene to carbon dioxide was known. The inhibitor reduces the ethylene conversion to

some extent (conversion meaning mol of ethylene reacting per mol of ethylene fed to the reactor) with as little unfavorable effect upon selectivity as possible and often provides a selectivity increase (selectivity being the mols of ethylene oxide formed per mol of ethylene reacting). Ideally, therefore, the inhibitor functions to reduce the amount of ethylene converted to carbon dioxide without reducing the amount of ethylene converted to ethylene oxide and thus, acts to increase yield, i.e. increase the number of mols of ethylene oxide formed per mol of ethylene fed.

Over the years, a number of such inhibitors have been found to be effective for these purposes, foremost amongst them being halogenated compounds, especially ethylene dichloride, mono- and dichlorobenzene and chlorinated biphenyls and polyphenyls (note U.S. patents 2,279,469 and 2,734,906). Whatever the inhibitor used, the amounts employed have uniformly been very small indeed. Generally, the amount of inhibitor added has been less than 0.5 parts of inhibitor by volume per million parts by volume of total material entering the reactor (hereinafter abbreviated as ppm) normally, less than 0.1 ppm and usually in the range of 0.01 to 0.05 ppm. In past practice, when the amount of inhibitor falls below the aforementioned ranges, the degree of inhibition falls, carbon dioxide formation increases, and reaction temperature may increase with great rapidity because of the much more exothermic nature of the carbon dioxide forming reaction in contrast to the ethylene oxide forming reaction. When amounts of inhibitor greater than about 0.5 ppm were used, over-inhibition occurred, i.e., catalyst activity was adversely affected, not only for carbon dioxide formation but also for ethylene oxide formation and, in extreme cases, the catalyst became completely inactive.

Prior art attempts to employ ethane as a substantial component of ethylene-containing reaction gases in ethylene oxide manufacture have heretofore been almost uniformly unsuccessful. With as little as 3% ethane in the reactor feed, conversion dropped radically and so also did production in terms of quantity of ethylene oxide produced per hour per unit volume of catalyst. Prior attempts to increase ethane content beyond even this minimal level have been abortive since reaction temperature control is quickly lost due to the phenomenon referred to as "hot-spotting" and, in extreme cases, the catalyst is so overheated as to be rendered wholly inactive.

In accordance with this invention, it has been discovered that ethane can be used in substantial concentration as a component of the reaction gases in ethylene oxide manufacture. The factor that makes such usage possible is the discovery that the amount of inhibitor employed must be significantly increased over that conventionally used and that the amount of inhibitor employed must be carefully keyed to the concentration of ethane and to the other reaction conditions employed. Accordingly, the process of this invention enables ethylene oxide to be produced by the direct catalytic oxidation of impure ethylene. Additionally, this process can provide even better temperature control than the processes of the prior art because of ethane's superiority to other materials as a reaction gas heat capacity modifier. The process of this invention is applicable to ethylene oxide production processes employing either air or high purity oxygen (85% oxygen or more) feedstocks as the source of molecular oxygen but it is particularly advantageous for use with high purity oxygen feedstocks.

In its broadest aspects the present invention relates to a process for the production of ethylene oxide by the silver catalyzed continuous oxidation of ethylene with molecular oxygen, wherein ethane is provided as a component of the total feed to the reaction in an amount of at least about 10 mol % of said feed in conjunction with a controlled amount of an inhibitor selected from ethylene dichloride, vinyl chloride, dichlorobenzene, monochlorobenzene, dichloromethane, and chlorinated phenyls, chlorinated bi-phenyls and chlorinated polyphenyls, the amount of inhibitor continuously added to the oxidation reaction mixture being between 20% and 300% of the amount determined from the equation:

$$I = kx$$

wherein: I is the inhibitor addition rate expressed in terms of parts of inhibitor added by volume per million parts by volume of oxidation reaction mixture; k is a constant which depends upon the nature of the chlorinated hydrocarbon inhibitor and is 1.0 for ethylene dichloride, 15.0 for vinyl chloride, 0.2 for dichlorobenzene, 1.0 for monochlorobenzene, 2.0 for dichloromethane and 5.0 for chlorinated phenyls, chlorinated biphenyls and chlorinated polyphenyls, and x is a factor determined by the equation:

$$\ln x = 103.5 - \left(\frac{54{,}000}{T}\right) + \ln\left(\frac{B+0.01}{50}\right) + 0.5 \ln E - 0.5 \ln (0.1F) + 0.5 \ln P$$

wherein:

T = reaction outlet gas temperature expressed in degrees Kelvin;

B = mol % ethane in the oxidation reaction mixture;

E = mol % ethylene in the oxidation reaction mixture;

F = flow rate expressed as lbs/hr/cu.ft. of catalyst;

P = reaction pressure in psia; and

ln is the symbol for the natural logarithm.

It is contemplated that the ethane employed in the process may be introduced by the ethylene feedstock, where ethane is present as an impurity therein, or the ethane may be introduced to the reaction gas from a separate source. It is further contemplated that ethane may be introduced to the reaction gas partially as an impurity in the ethylene feedstock and partially as an independent feed stream from a separate source. Regardless of how the ethane is introduced to the process, the process is operated in such manner as to achieve a relatively high concentration of ethane in the gas in the reaction zone. As a result of such operation higher productivities may be achieved by permitting the employment of higher oxygen concentrations. Since oxygen concentration influences selectivity and reaction rate, improved productivity may be obtained not only without attendant penalty but even with significant advantage. Further, as the ethane serves to moderate the peak reaction temperature, reaction selectivity may be improved. Employment of ethane in the reaction gas results in a substantial economic improvement over prior art processes wherein ethane is removed from feedstock preliminarily to catalytic oxidation of ethylene.

In accordance with a preferred embodiment, the invention contemplates the production of ethylene oxide by vapor phase reaction of ethylene and oxygen, wherein the feed to the reaction comprises ethylene, oxygen and at least 10 mol % ethane. Obviously, the concentration of oxygen in the reaction gas mixture must be such as to fall short of the flammable limit, that is, the concentration at which burning or even explosion may occur. This limit may also be regarded as the point where zero selectivity or complete oxidation initially can occur. Ethane permits broader ranges than the prior use of nitrogen, argon, or methane. Generally, it is preferred to use the highest oxygen concentrations which are practical in view of flammability considerations and in view of the necessity for providing a margin for inadvertent variations in operating conditions without exceeding the limit of flammability.

In the practice of the invention, components in the total feed to the reaction (hereinafter referred to as the "oxidation reaction mixture") expressed as mol or volume percent are:

	Broad	Desirable	Preferred
Ethylene	4—40	6—35	15—30
Oxygen	3—20	6—15	8—14
Ethane	10—80	20—70	40—60

The employment of ethane at such high concentrations in the oxidation reaction mixture with the advantageous results obtained is accomplished by conduct of the oxidation at conventional temperatures, pressures and flow rates but with inhibitor levels significantly different from those of the prior art. Moreover, these inhibitor levels are a complex function of the nature of the inhibitor to be used, the reaction conditions employed, and the composition of the oxidation mixture.

The amount of inhibitor employed is between 20% and 300% of that given by equation (1) below:

$$(1) \qquad\qquad I = kx$$

In equation (1) "I" is the inhibitor addition rate in parts by volume per million parts by volume of oxidation reaction mixture; k is a constant having a value dependent upon the nature of the inhibitor used; and x is a factor determined by the equation:

$$\ln x = 103.5 - \frac{54,000}{T} + \ln\left(\frac{B+0.01}{50}\right) + 0.5 \ln E - 0.5 \ln (0.1F) + 0.5 \ln P$$

wherein:

T = reaction outlet gas temperature expressed in degrees Kelvin;

B = mol % ethane in the oxidation reaction mixture;

E = mol % ethylene in the oxidation reaction mixture;

F = flow rate expressed as lbs/hr/cu.ft. of catalyst;

P = reaction pressure in psia; and,

ln is the conventional symbol for natural or Napierian logarithms.

Those inhibitors that we have found to be especially useful in our process are listed below as also are the value of K for each of these inhibitors:

Inhibitor	"k"
ethylene dichloride	1.0
vinyl chloride	15.0
monochlorobenzene	1.0
dichlorobenzene	0.2
dichloromethane	2.0
chlorinated phenyl, biphenyls and polyphenyls (see U.S. patent No. 2,734,906)	5.0

Of the foregoing inhibitors, we prefer to use ethylene dichloride because of its ready availability, low cost and ease of handling. Of course, mixtures of inhibitors can be used and, in such cases, the value of "k" is the weight of average value for the overall inhibitor composition added.

As stated, the amount of inhibitor to be added is within 20% and 300% of the value given by equation (1) above. In commercial operation however, we normally desire to add amounts of inhibitor between 50% and 150% of that calculated by equation (1) and we prefer to employ an amount of inhibitor which is between 70% and 130% of that calculated by equation (1). Within these ranges, it is, of course, possible for a given the amount of inhibitor employed for a given plant operation in order to obtain the optimum selectivity-conversion relationship for a given situation. Reaction conditions, including ranges of values for "T", "F" and "P" are discussed subsequently.

In one embodiment of the invention, when starting with a commercial ethylene fraction containing a substantial amount, at least 10 mol %, of normally gaseous paraffins having more than one carbon atom, the ethylene in its impure commercial form is fed directly into the reaction zone.

In the production of ethylene oxide by the silver-catalyzed controlled oxidation of ethylene with molecular oxygen in accordance with the invention, the reactants comprising ethylene, oxygen and ethane are passed over a catalyst containing metallic silver at conditions of temperature and pressure resulting in the reaction of ethylene and oxygen with the formation of reaction products comprising ethylene oxide.

Catalysts employed in the process of the invention comprise any of the silver metal-containing catalysts disclosed in the prior art capable of catalyzing the controlled oxidation, with molecular oxygen, of ethylene to ethylene oxide. These comprise the catalysts consisting essentially of silver metal upon a suitable support. Suitable supports comprise, for example, any of the siliceous and aluminous support materials heretofore employed. Particularly suitable catalysts comprise those consisting essentially of silver metal upon such supports as alundum, silicon carbide, silica carborundum and any of the many alumina supports. Suitable catalysts comprise, for example, those disclosed and claimed in the U.S. Patents 3,207,700 and 2,752,362. It is to be understood, however, that the present invention is in no way limited to the use of any specific silver metal-containing catalyst.

The silver metal catalyst used in the process of the invention may be in the form of a stationary bed, or it may be used in fluidized or suspended form. The process is applicable to the use of a plurality of catalytic oxidation zones, arranged in series or in parallel. When using a plurality of such zones, reactants and/or added ethane may be introduced into one or more thereof. Conditions within such zones need not be the same, but may be varied and reaction products may be separated, or not, between such zones. Any part, or all, of the reactants, ethane and/or diluent materials may be introduced into one or more of the reaction zones at more than one point thereof.

The controlled oxidation reaction may be carried out at temperatures in the range of from 150°C (423°K) to 300°C (573°K). Pressures in the range of from atmospheric to 650 p.s.i.a. are generally employed, while a range of from 200 to 450 p.s.i.a. is preferred. Higher pressures, may, however, be used within the scope of the invention. The flow rate of the oxidation reaction mixture may be broadly within the range of 100 lbs/hr/ft³ of catalyst to 1000 lbs/hr/ft³ of catalyst but is preferably within the range from 250 to 650 lbs/hr/ft³ of catalyst. Diluent materials such as, for example, nitrogen, carbon dioxide and steam, may be present in the oxidation reaction mixture in varying amounts in addition to the ethane. Such other diluents may be introduced into the oxidation reaction mixture from build-up within the recycles conventionally employed or separately introduced. They can be added to the system alone or together with ethane and/or unreacted ethylene recovered from the reactor effluent.

Molecular oxygen employed as reactant in the process may be obtained from any suitable source. The suitable oxygen charge may consist essentially of relatively pure oxygen or a concentrated oxygen stream comprising molecular oxygen in major amount with a lesser amount of one or more diulent inert gases such as, for example, nitrogen and argon. A preferred concentrated oxygen gas, suitable for use as the make-up oxygen reactant in the process of the invention, comprises the concentrated oxygen gas consisting essentially of oxygen, nitrogen and argon obtained, for example, from air by suitable separating means comprising one or more such steps as fractionation, low temperature distillation and other conventional separating means. The suitable oxygen-containing gas preferably has an oxygen concentration of at

least 85 mol %. Since the amount of gaseous materials which must be vented from the oxidation process varies directly with the increase in inert gaseous diluents introduced, if any, increase in materials vented is generally accompanied by a decrease in yield of ethylene oxide from ethylene feed, it is preferred to employ molecular oxygen gas having high oxygen concentrations, for example, from 85 to 99.9 mol %. Particularly preferred is the use of a concentrated oxygen gas containing from 90 to 99.9 mol % of molecular oxygen. The concentration of oxygen in the oxidation reaction mixture can vary within the scope of the invention. Generally oxygen concentration in the oxidation reaction mixture would be within the range from 3 mol % to 20 mol %, desirably within the range of 6 mol % to 15 mol %, preferably within the range of from 8 mol % to 14 mol % but as aforementioned, care must be exercised to maintain the oxygen concentration somewhat below the flammable limit for the specific conditions employed. Especially good results are obtained with an oxygen concentration of about 11—12 mol % and an ethane concentration of about 40—60 mol %.

The process of the invention can be practised with a relatively broad concentration of ethylene in the total charge of the reaction zone. Thus, ethylene can constitute, for example, broadly from 4 to 40 mol % of the total feed to the ethylene reaction zone. A concentration of ethylene in the total reactor feed of from 6 to 35 mol % is desirable, while 15 to 30 mol % is particularly preferred. Higher or lower ethylene concentrations can however be used within the scope of the invention. Maintaining a specifically desired ethylene concentration is facilitated by controlled addition of ethane and by control of the amount of materials, such as, for example, methane, nitrogen, carbon dioxide and argon, recycled from within the system.

It has been found that, contrary to the prior art, it is unnecessary to maintain a mol ratio of ethylene to oxygen in excess of 1 in the total feed to the reaction zone. Furthermore, irrespective of ethylene and oxygen relative concentrations, carbon steel reactor tubes may be used as well as alloy steel tubes.

Thus, the improved efficiency and productivity advantages attendant to the practice of the present invention are achieved with even less of the rigorous and complicated controls required by prior art processes.

Essential to the attainment of the objects of the invention is the inclusion of a substantial proportion of ethane, at least 10 mol % in the total feed to the ethylene reaction zone. The ethane introduced into the system may be obtainable from any suitable source. It should be noted that in contrast to the prior art methane process aforementioned, the presence of paraffinic hydrocarbons other than ethane is not detrimental to the attainment of the object of the present invention. Suitable sources of ethane comprise, for example, natural gas and normally gaseous by-product streams containing ethane with or without other paraffins, obtained in thermal hydrocarbon conversion processes. Where ethane is introduced into the system from an independent source, it may be combined directly with a part or all of the make-up ethylene, the recycle stream or with the feed at the point of entry into the oxidation zone. A part or all of such ethane entering the system may be introduced as a separate stream into the reaction zone along one or more points along the length thereof.

The invention is now illustrated by the following Examples.

Control

The first ethylene oxide run was conducted for the purpose of providing a standard or reference base where substantially no ethane is contained in the total feed to the ethylene oxidation zone. In this run ethylene was oxidized to ethylene oxide by reacting ethylene with molecular oxygen in the presence of a supported silver metal catalyst at a temperature of 250°C and a pressure of 315 p.s.i.a. The make-up ethylene charge consisted essentially of 100% ethylene at a flow rate of 1.14 pounds per hour. The make-up oxygen gas charge consisted essentially of 99.5% oxygen and had a flow rate of 1.66 lbs per hour. An independent fresh nitrogen charge, substantially 100% nitrogen, at a flow rate of 0.01 pounds per hour, completed the make-up charge streams. To the make-up gas streams, recycle gas, at a flow rate of 50.7 lbs per hour, was added. This recycle gas had a molar composition of 15.2% ethylene, 4.6% oxygen, 7.4% carbon dioxide, 32% argon, and 40.8% nitrogen. Resultant total feed to the reactor, which contained 0.1 ft³ of catalyst, flowed at a rate of 53.5 lbs per hour and had a molar composition of 17% ethylene, 7.5% oxygen, 7% carbon dioxide, 30% argon and 38.5% nitrogen. To this feed was added 0.5 ppm by volume of ethylene dichloride. Ethylene oxide was recovered from the reactor effluent by absorption in water followed by distillation of the rich aqueous absorbate. Residual reactor gaseous effluence, free of reaction products comprising ethylene oxide, was returned as the recycle gas to the reaction with the exception of a small constant bleed from the system. Determination of the difference between the outlet and inlet ethylene oxide at the reactor provided a ΔEO of 1.75. The ΔEO value is commonly employed as a yardstick since it is proportional to ethylene oxide productivity and is readily measured

by chromatographic techniques. The overall yield of this run was 68.6%.

EXAMPLE 1

A first run in accordance with the invention was conducted with the ethane present in the total feed in substantial amount as a ballast. In this run make-up ethylene charge, comprising essentially 100% ethylene, was employed at a flow rate of 1.31 lbs per hour. The make-up oxygen gas charge, comprising essentially 99.5% oxygen, was employed at a flow rate of 1.87 lbs per hour. The third and final charge stream consisted essentially of 100% ethane gas at a flow rate of 0.02 lbs per hour. A recycle gas, at a flow rate of 50.3 lbs per hour was mixed with the make-up streams. The molar composition of the recycle gas comprised 15.2% ethylene, 8.0% oxygen, 7.5% carbon dioxide, 17% argon and 52.3% ethane. Resultant total feed, at a flow rate of 53.5 lbs per hour was introduced to the reactor, which contained the same amount and type of catalyst and was maintained at the same temperature and pressure conditions as the Control. The molar composition of the total feed was 17% ethylene, 11% oxygen, 7% carbon dioxide, 16% argon and 49% ethane. Ethylene dichloride inhibitor in an amount of 15 ppm by volume was added to the reaction gas. The ΔEO value determined for this run was 1.92, while the overall yield was 68.6%.

When an attempt is made to repeat this Example employing the same amount of inhibitor as used in the Control, it is found that excessive hot-spotting occurs and that the reaction results only in the production of CO_2. Attempting to repeat Example 1 with 200 ppm of inhibitor results in a very much lower ΔEO and consequently a much reduced yield.

An attempt to repeat the Control at the same inhibitor levels as used in Example 1 results in an extremely rapid catalyst activity decline with the ΔEO quickly falling to zero. If inhibitor addition rates are not quickly reduced to the approximate levels of the Control, the catalyst may be irreversibly poisoned.

When Example 1 is repeated employing the same addition rates of monochlorobenzene, or 225 ppm of vinyl chloride or 3 ppm of dichlorobenzene or 30 ppm of dichloromethane, comparable results are obtained.

EXAMPLE 2

A second run in accordance with the invention with ethane present in the total feed, in substantial amount as ballast, but with an increased ethylene concentration was also conducted at the same reaction conditions as in Example 1. The make-up ethylene charge in this run consisted essentially of 100% ethylene at a flow rate of 1.45 lbs per hour. The make-up oxygen gas charge consisted essentially of 99.5% oxygen and had a flow rate of 2.08 lbs/hr. An independent make-up charge of essentially 100% ethane, at a flow rate of 0.02 lbs per hour was also employed. A recycle gas, at a flow rate of 49.95 lbs per hour was mixed with the make-up charge streams. This recycle gas has a molar composition of 23.6% ethylene, 7.7% oxygen, 7.6% carbon dioxide, 14% argon and 47.1% ethane. The total feed to the reactor, at a flow rate of 53.5 lbs per hour, had a molar composition of 25% ethylene, 11% oxygen, 7% carbon dioxide, 13% argon, and 44% ethane. Ethylene dichloride in an amount of 15 ppm by volume was introduced to the reactor as an inhibitor. The ΔEO value for this run was determined to be 2.13 while the overall yield was 68.6%.

The total reactor feed compositions and results of the foregoing reference and invention runs are set forth, for ease of comparison, in Table 1:

TABLE I

	Prior Art Control	Invention Ex. No. 1	Ex. No. 2
Ethylene	17	17	25
Oxygen	7.5	11	11
Carbon Dioxide	7	7	7
Argon	30	16	13
Nitrogen	38.5	—	—
Ethane	—	49	44
Ethylene Dichloride	0.5 ppm	15 ppm	15 ppm
ΔEO	1.75	1.92	2.13
Overall Yield	68.6%	68.6%	68.6%

NOTE: Components of reaction gas mixture are given in terms of mol or volume percent except ethylene dichloride which is in terms of parts per million by volume.

It should be noted that the amount of inhibitor predicted for use in the foregoing Examples 1 and 2 by use of equations (1) and (2) above are respectively 12.6 ppm and 13.6 ppm, both of which values are within the claimed range of 20% to 300% of the values calculated by the equations.

When employing an oxidation reaction mixture having the composition of Example 2 in a commercial plant under conditions similar to that of Example 2 save only that reaction temperature employed was 240—245°C, the predicted inhibitor addition rate and the actual results agreed within 15%.

Examination of the results in Table I indicates conclusively that the utilization of ethane as a major component of the total feed provides a significant improvement in

productivity of ethylene oxide, of the order of 10%, without any sacrifice in overall yield. This improvement is apparently directly attributable to the increased oxygen concentration in the reaction gas mixture. It will be noted from Run No. 2 that where inlet reaction conditions are substantially the same, with the sole exception of increased ethylene concentration in the reaction gas mixture, even further improvement in ethylene oxide productivity is obtained, the productivity improvement in Run No. 2 being of the order of 22%.

WHAT WE CLAIM IS:—

1. In a process for the production of ethylene oxide by the continuous controlled oxidation with molecular oxygen of ethylene contained in an oxidation reaction mixture in the presence of a silver catalyst, the improvement which comprises; employing ethane as a component of the oxidation reaction mixture, the concentration of ethane in the oxidation reaction mixture being at least 10 mol %, in conjunction with a controlled amount of an inhibitor selected from ethylene dichloride, vinyl chloride, dichlorobenzene, monochlorobenzene, dichloromethane, and chlorinated phenyls, chlorinated bi-phenyls and chlorinated polyphenyls, the amount of inhibitor continuously added to the oxidation reaction mixture being between 20% and 300% of the amount determined from the equation:

$$I = kx$$

wherein: I is the inhibitor addition rate expressed in terms of parts of inhibitor added by volume per million parts by volume of oxidation reaction mixture; k is a constant which depends upon the nature of the chlorinated hydrocarbon inhibitor and is 1.0 for ethylene dichloride, 15.0 for vinyl chloride, 0.2 for dichlorobenzene, 1.0 for monochlorobenzene, 2.0 for dichloromethane and 5.0 for chlorinated phenyls, chlorinated bi-phenyls and chlorinated polyphenyls; and, x is a factor determined by the equation:

$$\ln x = 103.5 - \left(\frac{54{,}000}{T}\right) + \ln\left(\frac{B + 0.01}{50}\right) + 0.5 \ln E - 0.5 \ln (0.1F) + 0.5 \ln P$$

wherein:

T = reaction outlet gas temperature expressed in degrees Kelvin;

B = mol % ethane in the oxidation reaction mixture;

E = mol % ethylene in the oxidation reaction mixture;

F = flow rate expressed as lbs/hr/cu.ft. of catalyst;

P = reaction pressure in psia; and

ln is the symbol for the natural logarithm.

2. A process as claimed in claim 1 wherein T is between 423°K and 573°K, E is between 4%. and 40%, F is between 100 lbs/hr/cu.ft. of catalyst and 1000 lbs/hr/cu.ft. of catalyst and P is between 200 p.s.i.a. and 450 p.s.i.a.

3. A process as claimed in claim 1 or claim 2 wherein the amount of inhibitor is between 50% and 150% of that calculated by the equations in claim 1.

4. A process as claimed in claim 3, wherein the amount of inhibitor is between 70% and 130% of that calculated by the equations in claim 1.

5. A process as claimed in any of claims 1 to 4 wherein the inhibitor is ethylene dichoride.

6. A process as claimed in any of claims 1 to 5 wherein oxygen is supplied to the reaction mixture as high purity oxygen containing at least 85 mol % oxygen.

7. A process as claimed in any of claims 1 to 6 wherein the oxidation reaction mixture comprises:

Ethylene	4—40 mol %
Oxygen	3—20 mol %
Ethane	10—80 mol %

8. A process as claimed in claim 7 wherein the oxidation reaction comprises:

Ethylene	6—35 mol %
Oxygen	6—15 mol %
Ethane	20—70 mol %

9. A process as claimed in claim 8 wherein the oxidation reaction mixture comprises:

Ethylene	15—30 mol %
Oxygen	8—14 mol %
Ethane	40—60 mol %

10. A process as claimed in claim 9 in which the oxygen forms 11 to 12 mol % of the oxidation reaction mixture.

11. A process as claimed in claim 10 wherein the oxidation reaction mixture comprises:

Ethylene	17 mol %
Oxygen	11 mol %
Ethane	49 mol %

12. A process as claimed in claim 10 wherein the oxidation reaction mixture comprises:

Ethylene	25 mol %
Oxygen	11 mol %
Ethane	44 mol %

13. A process according to claim 1 for the production of ethylene oxide by the continuous silver catalyzed controlled oxidation with molecular oxygen of ethylene contained in an oxidation reaction mixture which also contains ethane and an inhibitor, substantially as hereinbefore described.

14. A process according to claim 1 for the production of ethylene oxide by the continuous silver catalyzed controlled oxidation with molecular oxygen of ethylene contained in an oxidation reaction mixture which also contains ethane and an inhibitor, substantially as shown in Examples 1 and 2.

15. Ethylene oxide prepared by the process claimed in any of claims 1 to 14.

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